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ABSTRACT

Experiments have been conducted to help establish the source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) that are produced during bleaching of pulp with high levels of chlorine. Conditions have been established for observing the progressive development of ring chlorination of dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) which were adsorbed onto cotton linters. The distribution and types of mono-, di-, tri-, and tetra-chlorinated dibenzofurans produced as a function of time for the chlorination of DBF-spiked cotton linters were similar to that obtained from chlorination of an extracted pulp; this result indicates that DBF is probably the principal PCDF precursor in pulp. Because of the greater reactivity of DBD upon chlorination, few lower chlorinated PCDD were observed and the mechanism of PCDD formation is less clear.

INTRODUCTION

The bleaching of wood pulp by chlorination appears to lead to low levels of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F). Both the chlorine and paper industries have been studying ways to reduce the levels of PCDD/F in paper products and mill discharges. The most studied PCDD/F are 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and dibenzofuran (2,3,7,8-TCDD and 2,3,7,8-TCDF) because of their significant toxicity.[1]

Research has suggested that DBD/F are present in wood pulp and that the chlorination of DBD/F is responsible for a significant portion of the observed PCDD/F. Chlorination of DBD/F gives

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Other mechanisms of PCDD/F formation in pulp bleaching may lead to direct formation of tetra-CDD/F -- omitting sequential formation of the mono-, di-, and tri-CDD/F structures; these mechanisms might also produce unusual isomer patterns. An example mechanism of this type is the chlorination and then coupling of lignin units to directly produce a tetra-CDD. Another is the chlorination of DBD/F precursors which are chemically bound to lignin; several chlorine substitutions would probably occur before detachment from the lignin.[11]

If DBD/F chlorination were the only mechanism of PCDD/F formation, it might be possible to remove or destroy these precursors before employing chlorine bleaching and thereby produce a pulp which contains no PCDD/F. However, if other pathways exist, such as formation from lignin, the only control measure may be to reduce or eliminate the amount of applied chlorine. Chlorine, however, appears to be the most effective and least costly bleaching agent for selectively delignifying wood pulp.

Our research was aimed at further examining the mechanisms of PCDD/F formation during pulp bleaching by comparing the distribution and isomer patterns of mono-, di-, tri-, and tetra-CDD/F as a function of chlorination time. Experiments were conducted with both cotton linters and an extracted wood pulp. The cotton linters were chosen as an experimental matrix because of close similarities to pulp fibers, the absence of lignin, and the lack of analytical interferences found in pulp.

EXPERIMENTAL

Chlorination of Cotton Linters

Cotton linters were pre-extracted with an ethanol:toluene (2:1) solution for approximately 18 hours in Soxhlet apparatus and then mixed with reagent water and dried overnight in a lyophilizer. Approximately 5 g of dried, pre-extracted linters were added to each of 11 wide-mouth glass sample bottles located on a tumbling apparatus. One bottle was labeled as the

Process Blank. The dried linters in each bottle were spiked with 150 ng of DBD and DBF (30 ng/g) dissolved in 5 mL of methanol; the methanol was gradually removed from the samples using a vacuum pump.

A 250-mL aliquot of reagent water was added to each of the 11 bottles. Next, concentrated HCl was added to achieve a final concentration of 0.2M HCl. A 250-mL aliquot of chlorine water was added to each bottle except the Process Blank. The concentration of the chlorine water was 0.05 mg/mL chlorine, totaling 12.5 mg of chlorine or 0.25 percent chlorine per cotton linters. Immediately after the addition of the chlorine water, the bottles were capped and tumbled. Duplicate samples were removed from the tumbling apparatus at 10 min, 20 min, 40 min, 70 min, and 2 hr. The Process Blank was removed after 2 hr. Immediately after removal, aqueous sodium thiosulfate was added to the bottles to quench the residual chlorine remaining in the samples. The chlorine level in the 2 hr duplicate samples was measured prior to quenching using a titrimetric technique.[12]

Preparation of Cotton Linters Samples for Analysis

After chlorination, the linters samples were vacuum filtered. The dried linters were transferred to Soxhlet apparatus thimbles, mixed with 80 g of anhydrous sodium sulfate, and spiked with the following internal standards: DBF-$^{13}C_{12}$ (5 ng/g), DBD-$^{13}C_{12}$ (1 ng/g), 2,3,7,8-TCDF-$^{13}C_{12}$ (1 ng/g), and 2,3,7,8-TCDD-$^{13}C_{12}$ (1 ng/g). The spike levels were based on dry weights. The spiked linters were extracted for approximately 18 hr with benzene. The resulting extracts were concentrated to 3-5 mL using macro Kuderna-Danish (K-D) distillation techniques. The aqueous portions of the chlorinated linters samples were transferred to 1-L separatory funnels and extracted with three 60-mL portions of methylene chloride. The resulting aqueous extracts were dried over anhydrous Na_2SO_4 and reduced in volume. The aqueous and linters extracts for individual samples were combined, concentrated, and solvent exchanged to hexane.

The sample extracts in hexane were processed through dual 5 g basic alumina columns. The columns were eluted with 15 mL of 3% CH_2Cl_2/hexane and 40 mL of 50% CH_2Cl_2/hexane. The

40-mL 50% CH_2Cl_2/hexane fractions from the dual columns were concentrated to approximately 100 uL and spiked with d_{10}-fluorene as a recovery standard.

Chlorination of Unbleached Pulp

A preliminary chlorination experiment was conducted with two pre-extracted pulp samples, a Process Blank (omission of chlorine only), and a Chlorine Check Sample (pulp and chlorine water). The purpose of the preliminary experiment was to determine if: (1) sufficient chlorine was available for a 2-hr pulp chlorination; (2) the pulp chlorination rate was appropriate; (3) the amount of pulp provided detectable levels of mono- through tetra-CDD/CDF; and (4) the dual alumina column cleanup used for the linters samples was appropriate for pulp samples. The chlorination procedures used for this preliminary experiment were the same as those used for the linters experiments except that the sample weight was increased from 5 g of linters to 30 g of pulp, and the chlorine level was increased from 0.25% chlorine on linters to 10% chlorine on pulp. The chlorine level was monitored in the preliminary pulp experiment by removing an aliquot from the Chlorine Check Sample several times during the chlorination period and determining the chlorine level in the sample aliquot by titrimetric techniques. The results, as shown below, indicate that sufficient chlorine remained in the experimental system to continue pulp chlorination throughout the 2 hr period.

Chlorine Level

Time	(mg/mL)
0 min	3.2
10 min	0.79
20 min	0.54
60 min	0.29
2 hr	0.15

For the timed chlorination experiment, pulp was pre-extracted with ethanol:toluene (2:1) for approximately 18 hr in a Soxhlet apparatus, mixed with reagent water, and dried overnight in a lyophilizer. Approximately 30 g of dried, pre-extracted pulp was added to each of 14 wide-mouth glass sample bottles assembled on a tumbling apparatus. One bottle was labeled as the Process Blank and one bottle was labeled as the Chlorine Check Sample. A 1-L aliquot of chlorine water (concentration 3.5 mg/mL; total of 3.5 g of chlorine or 12 percent chlorine per pulp) was added to each sample, except the Process Blank. A 1-L aliquot of reagent water was added to the Process Blank. Immediately after the addition of the chlorine water, the bottles were capped and tumbled. Replicate samples were removed from the tumbling apparatus at 10 min, 20 min, 40 min, 70 min, and 2 hr. The Process Blank was removed after 2 hr. Immediately after removal, the excess chlorine in the samples was quenched by adding aqueous sodium thiosulfate to the samples.

Preparation of Pulp Samples for Analysis

After chlorination, the pulp samples were vacuum filtered. The dried pulp from each sample was split into half and each half extracted separately. The pulp samples were mixed with anhydrous sodium sulfate, spiked with DBD/F-$^{13}C_{12}$ and TCDD/F-$^{13}C_{12}$ internal standards, and extracted in Soxhlet apparatus for 18 hr with benzene. The volume of the resulting pulp extracts was reduced using K-D distillation. The aqueous portions of the pulp samples were transferred to 1-L separatory funnels and extracted with three 60-mL portions of CH_2Cl_2. During liquid/liquid extraction, an emulsion formed in most samples which made separation of the organic layer from the aqueous layer difficult. Samples were centrifuged to enhance separation. The resulting aqueous extracts were dried over anhydrous Na_2SO_4 and concentrated to approximately 1 to 2 mL using K-D distillation.

The aqueous and pulp extracts for individual samples were combined and concentrated to approximately 1 mL using micro-K-D techniques. Concentrated sample extracts were processed through various cleanup procedures including alumina and carbon columns to remove analytical interferences. Acid/base washing and acid/base silica column cleanup techniques typically used

in PCDD/F analysis[13,14] could not be used for these samples because preliminary experiments conducted for this work showed loss of DBD/F with these cleanup procedures. Most samples were processed through a final cleanup procedure consisting of a 20 g basic alumina column, followed by a 5 g basic alumina column. Analyte recovery was demonstrated prior to use of cleanup techniques.

Analytical Procedures

Linters and pulp sample extracts were analyzed for DBD/F and mono- through tetra-CDD/F by combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/MS), employing a Hewlett Packard Model 5890 gas chromatograph interfaced directly into the ion source of a VG Model 70SEQ high resolution mass spectrometer. A 60 m DB-5 capillary column with helium as the carrier gas was used to separate PCDD/F. The GC column temperature was programmed as follows: 75°C isothermal for 2 min, a 15°C/min ramp to 190°C, followed by an 8°C/min ramp to 310°C. The injection port and transfer line between the gas chromatograph and the mass spectrometer were held at 300°C. The mass spectrometer was operated in the electron capture, negative ionization mode, with an ion source temperature of 250°C.

HRGC/MS data were acquired using a VG Model 11-250J data system. PCDD/F were detected by selected ion monitoring of two ions of the most intense chlorine isotope cluster of each PCDD/F congener group. Identification criteria included: 1) simultaneous response at both ion masses; 2) chlorine isotope ratios within 20 percent of the theoretical value; 3) retention times near retention times of available $^{13}C_{12}$-analog and native standards; and 4) signal-to-noise ratio equal to or greater than 2.5 to 1. An initial three-point calibration curve was established in duplicate for the HRGC/MS system; this calibration curve was verified each day of operation prior to analysis of samples. Native and recovery response factors were generated from this initial calibration and used in data calculations.

Quantitation was based on comparison of the combined peak areas of the quantitation ions to the peak areas detected for a known amount of internal standard, considering the daily calculated response factors. All PCDD/F were quantitated as homologues. The areas for DBD/F were compared to DBD/F-$^{13}C_{12}$ internal standards. The areas for mono-CDD/F through tetra-CDD/F were compared to tetra-CDD/F-$^{13}C_{12}$ internal standards. Internal standard recoveries were monitored for each sample by comparing the combined peak areas for the internal standards to the peak area detected for a known amount of the d_{10}-phenanthrene recovery standard. In most cases, recoveries were between 50-150%. Samples with recoveries outside these limits were excluded from reported data or qualified.

RESULTS AND DISCUSSION

Evaluation of Background Dibenzofuran

Dibenzofuran is known to be a general laboratory contaminant and can be found in common laboratory solvents and reagents. Estimated amounts of the various solvents to be used in the sample analyses were combined, concentrated, and analyzed; 300-600 pg of DBF and no DBD were detected. This background level corresponded to approximately 0.5 ng/g DBF for a 1 g sample. Consequently, spike levels of 10 ng/g DBF and 1 ng/g DBD were selected for the first chlorination experiments to insure reasonable levels of DBD/F above background amounts.

Determination of PCDD/F Distribution Between Solid/Aqueous Phases

An initial experiment was conducted to determine the distribution of PCDD/F formed in chlorination experiments between solid and aqueous phases of chlorination samples. The purpose of this experiment was to determine if both solid and aqueous phases of subsequent chlorination samples needed to be prepared for analysis.

Linters samples were chlorinated for 2 hr as previously described for this experiment. Duplicate linters samples were spiked with DBD and DBF at 1 and 10 ng/g, respectively, prior to chlorination. Duplicate unspiked linters samples were also chlorinated. Chlorinated linters samples were prepared for analysis, as previously described, except that linters and aqueous extracts from the chlorination samples were not combined but were analyzed separately. Alumina column cleanup was conducted on the aqueous extracts but not on the linters extracts.

Chlorine-containing DBD/F products were detected in both linters and aqueous extracts in the chlorination samples from this initial experiment (Table 1). The distribution appeared to favor the linters for all but DBD and DBF. As a result, both sample portions were extracted separately but combined for analysis in future experiments. In addition, a higher DBD/F spike level was used in future linters chlorination experiments to ensure that measurable PCDD/F were formed.

PCDD/F Formation During Linters Chlorination

A mild chlorination of DBD/F-spiked cotton linters was conducted over 10, 20, 40, 70, and 120 min. The data for the appearance and disappearance of DBD/F and mono- through tetra-CDD/F for the chlorinated linters samples displayed several interesting trends as shown in Figures 1-3 and Table II.

The majority of DBD/F spiked into these samples at 30 ng/g prior to chlorination seems to be consumed within the first 10 minutes of chlorination (Fig. 1). The levels of DBD/F remained nearly constant after 10 min of chlorination. The DBF concentration of approximately 10 ng/g observed after 10 min matched the estimated level of background DBF contamination associated with the chlorination process as determined by a Process Blank. The Process Blank consisted of a pulp sample processed through the chlorination procedure without addition of chlorine water. The slow decrease with time of the extremely low DBD levels appears to be a real effect.

The chlorination patterns of Figures 2 and 3 indicate that *DBD is more reactive towards chlorine than is DBF*. The data also suggest that the lower chlorinated components form before higher chlorinated ones suggesting a *progressive chlorination of DBD and DBF*. Straight lines were drawn between data points on the plots shown in Figures 2 and 3. Since no data was collected from 0-10 minutes, the curve shapes in this area, as shown, may be misleading; for example, in the first 10 minutes there is probably a steep rise and fall in mono-CDF and mono and di-CDD concentrations (Figures 1 and 2).

The DBD/F equivalents are also presented in Table II. The DBD/F equivalents were calculated by multiplying the mono- through tetra-CDD/F concentrations by a ratio of the PCDD/F molecular weight to the DBD/F molecular weight and summing the resulting DBD/F equivalents calculated for all congener classes. The DBF equivalents for these samples rose with time. After 70 min, the DBF equivalent for the chlorinated samples was approximately the same as the DBF concentration in the Process Blank. However, the DBD equivalent remained relatively constant over the entire chlorination period and was much lower than the DBD level measured in the Process Blank of 20 ng/g. The data suggest that some DBD may have reacted to form higher chlorinated dioxins or other compounds not detected in the analysis.

More tetra-CDF isomers than tetra-CDD isomers were observed at all chlorination times. For both tetra-CDF and tetra-CDD, the 2,3,7,8-substituted isomer was the most prominent as shown in Figure 4. This isomer distribution pattern is typical for bleached pulp.[3] The second prominent tetra-CDF isomer in Figure 4 is likely 1,2,7,8-TCDF, which is a known marker for bleached pulp.[15]

The data suggest that probably no one experimental condition will exist which will allow observation of the progressive development (rise and fall) of mono- through tri-CDD/F. The conditions selected for the progressive development of mono- through tetra-CDF in spiked cotton linters were ideal. Because of the greater reactivity of DBD, however, the distribution of DBD products was skewed towards the higher chlorinated products. Additional experiments for finding conditions for obtaining ideal mono- through tetra-CDD profiles were not conducted.

PCDD/PCDF Formation During Pulp Chlorination

The next step was to determine the distribution of mono-, di-, tri-, and tetra-CDD/F as a function of chlorination time for pre-extracted unspiked pulp. A preliminary experiment was conducted to determine the best chlorination conditions for pulp. Since the lignin in the pulp was expected to react rapidly with chlorine, higher levels of chlorine and a larger sample size were employed for the pulp experiment than for the linters experiment, as previously described.

In the pulp chlorination experiment, mono-, di, and tri-CDD were not observed in the chlorinated pulp samples at any chlorination time. Because of the higher chlorine level and higher reactivity of DBD (compared to DBF), the chlorination appears to have proceeded past the lower chlorinated PCDD. Most likely, lower PCDD products were formed during the first 10 minutes of the experiment, where measurements were not recorded. Tetra-CDD was observed and increased with chlorination time as shown in Figure 5. The tetra-CDD formation pattern was similar to the formation pattern observed for the spiked linters.

The progressive formation of PCDF observed with DBD/F-spiked cotton linters was also observed with the pre-extracted unspiked pulp. Mono-, di-, and tri-CDF concentrations appeared to decrease with increasing chlorination time as shown in Figure 6 for mono-CDF. Decreases in di- and tri-CDF concentrations were more gradual and occurred later in the chlorination period than decreases in mono-CDF concentrations. However, tetra-CDF appeared to increase with chlorination time. As with PCDD, the higher chlorine level used in the pulp chlorination appeared to have led to a more rapid chlorination of the DBF components; the latter stages of the reaction appeared to dominate.

Overall, *the data suggests a progressive development of chlorinated DBF products. There are no unusual trends which suggest another type of dioxin precursor is present in the pulp.*

The PCDD/F concentrations formed by chlorination of DBD/F were expected to be in the low part per trillion range for the pulp experiment. This expectation was met for tetra-CDD.

However, PCDF concentrations were at low part per billion levels which was much higher than expected. This observation, together with the progressive development of mono- through tetra-CDF, suggests that the pulp still contained significant amounts of DBF, that DBF was present as a contaminant, or DBF was formed during chlorination. A process blank sample analyzed with these chlorinated pulp samples contained ppb levels of DBF suggesting that the *thoroughly extracted pulp still contained DBF.* One can speculate that the DBD/F are absorbed strongly to lignin or that there are inaccessible regions in the pulp where DBD/F are trapped until freed during chlorination.

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REFERENCES

1. Tschirley, F.H. Scientific American, **1986**, 254, 29.

2. Voss, R. H., Luthe, C. E., Fleming, B. I., Berry, R. M., Allen, L. H., Presented at 1988 CPPA Environment Conference, Vancouver, B. C., Oct. 25-26, 1988.

3. Berry, R. M., Fleming, B. I., Voss, R. H., Luthe, C. E., Wrist, P. E. Presented at 75th Annual Mtg. CPPA Tech. Sect., Montreal, Quebec, Jan. 31-Feb. 3, 1989.

4. Gray, A. P., Dipinto, V. M., Solomon, I. J. J. Org. Chem. **1976**, 41, 2428; Gray, A. P., Cepa, S. P., Solomon, I. J., Aniline, O. *ibid.*, 2435.

5. Rappe, C., Swanson, S. E., Glas, B., Kringstad, K. P., de Sousa, F., Johansson, L., Abe, Z. Pulp Paper Can., in press.

6. LaFluer, L. E., Brunck, R., Ramage, K., McDonough, T. J., Malcolm, E.W. Presented at DIOXIN '89, Toronto, Ontario, Sept. 21, 1989.

7. Nonni, A. API/NCASI Dioxin Research Working Group Mtg., June 30, 1988.

8. Thompson, S. N. Appleton, Wisconsin, personal communication.

9. Hrutfiord, B. F., Negri, A.R. 1990 TAPPI Pulping Conference, **1990**, Toronto, Ontario, Oct. 14-17, p. 417.

10. Hise, R. G., Swanson, S. E., Wright, B. T. Chemosphere, **1990**, 20, 1723.

11. Shen, X., van Heiningen, A. 6th Intern. Symp. on Wood and Pulping Chem., Melbourne, Australia, April 30, 1991, Extended Abstracts, 557.

12. Greenberg, A. E., Trussell, R. R., Clesceri, L. S., Eds. Standard Methods for the Examination of Water and Wastewater, **1985**, 16th Edition, 294-300.

13. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Industrial Technology Division, Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision A, April, 1990.

14. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, SW-846, Test Methods for Evaluating Solid Waste, Method 8290: Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry, Revision 0, November, 1990.

15. Rappe, C., Lindstrom, G., Glas, B., Lundstrom, K., Borgstrom, S., Chemosphere, **1990**, 20, 1649-1656.

Table I. PCDD/F Concentration in Solid and Aqueous Sample Phases (ng/g)[a]

Analyte	DBD/F-Spiked Linter Sample			Duplicate DBD/F-Spiked Linter Sample			Unspiked Linter Sample			Duplicate Unspiked Linter Sample		
	Linter[b]	Aqueous	Linter/ Aqueous Ratio	Linter	Aqueous	Linter/ Aqueous Ratio	Linter	Aqueous	Linter/ Aqueous Ratio	Linter	Aqueous	Linter/ Aqueous Ratio
DBF	2.9	7.1	0.4	3.6	7.2	0.5	4.6	7.0	0.7	4.1	5.2	0.8
DBD	0.007	0.004	2	0.004	0.003	1	--	0.003	--	--	0.002	--
Mono-CDF	0.28	0.003	100	0.97	0.012	81	0.19	--	--	0.27	0.007[c]	40
Mono-CDD	--	--	--	--	--	--	--	--	--	--	--	--
Di-CDF	2.6	0.85	3.1	1.4	0.63	2.2	0.68	0.55	1.2	1.1	0.26	4.2
Di-CDD	--	--	--	--	--	--	--	--	--	--	--	--
Tri-CDF	4.1	0.38	11	2.5	0.28	8.9	1.1	0.085	13	1.3	0.081	16
Tri-CDD	0.19	0.012	16	0.080	0.009	9	--	--	--	--	--	--
Tetra-CDF	0.15	0.003	50	0.17	0.005[c]	30	0.048	--	--	--	--	--
Tetra-CDD	0.084	0.003	30	0.071	0.003	20	--	--	--	--	--	--

[a] "--" indicates analyte not detected above estimated method detection limit of 0.002 ng/g.

[b] Tetra-CDD-$^{13}C_{12}$ recovery was 38 percent.

[c] Mass ratio for analyte did not meet method limits due to low level detected.

Table II. Results for Linter Chlorination (ng/g)[a]

Analyte	10 min	20 min	40 min	70 min[c]	2 h[c]	Process Blank
DBF[b]	7.4	10	8.7	9.6	11	36
DBD[b]	0.26	0.18	0.11	0.09	0.06	20
Mono-CDF	2.8	1.4	0.30	0.48	0.48	--
Mono-CDD	--	--	--	--	--	--
Di-CDF	19	21	24	28	22	--
Di-CDD	2.8	2.0	0.86	0.75	0.08	--
Tri-CDF	4.0	6.3	12	18	34	0.01
Tri-CDD	7.0	7.7	7.2	6.4	4.4	0.01
Tetra-CDF	0.05	0.16	0.41	1.0	3.3	--
Tetra-CDD	1.7	2.9	3.6	5.2	8.0	0.004
DBD/DBF Equivalent						
DBF	18	20	25	32	38	
DBD	7.5	8.1	7.3	7.9	7.5	

[a] "--" indicates analyte not detected; results are duplicate averages except where indicated.

[b] Process blank and samples spiked with 30 ng/g linter DBD/DBF.

[c] Results represent single data point rather than average.

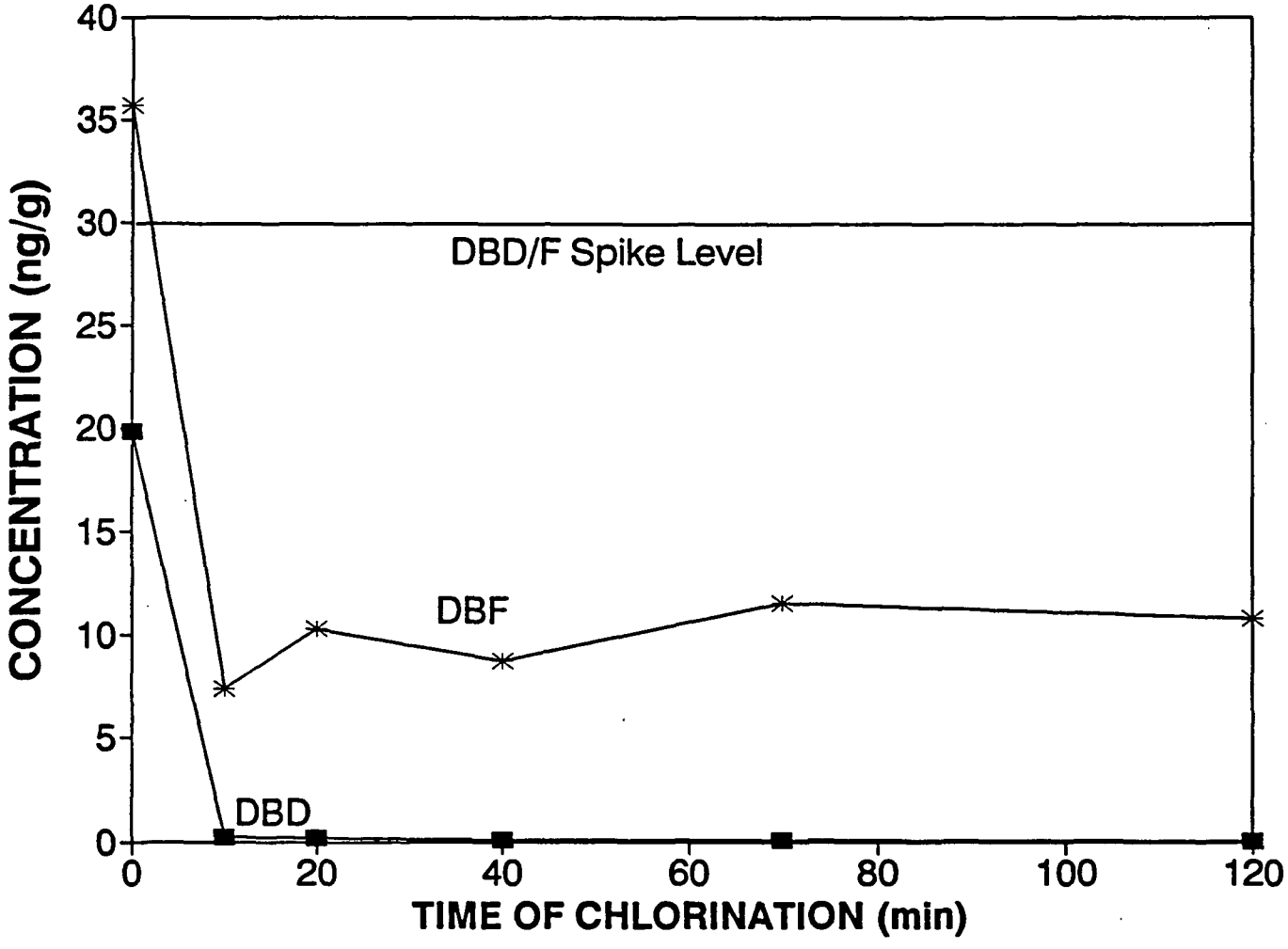

Figure 1. DBD/F Reduction Upon Chlorination of DBD/F-Spiked Linters

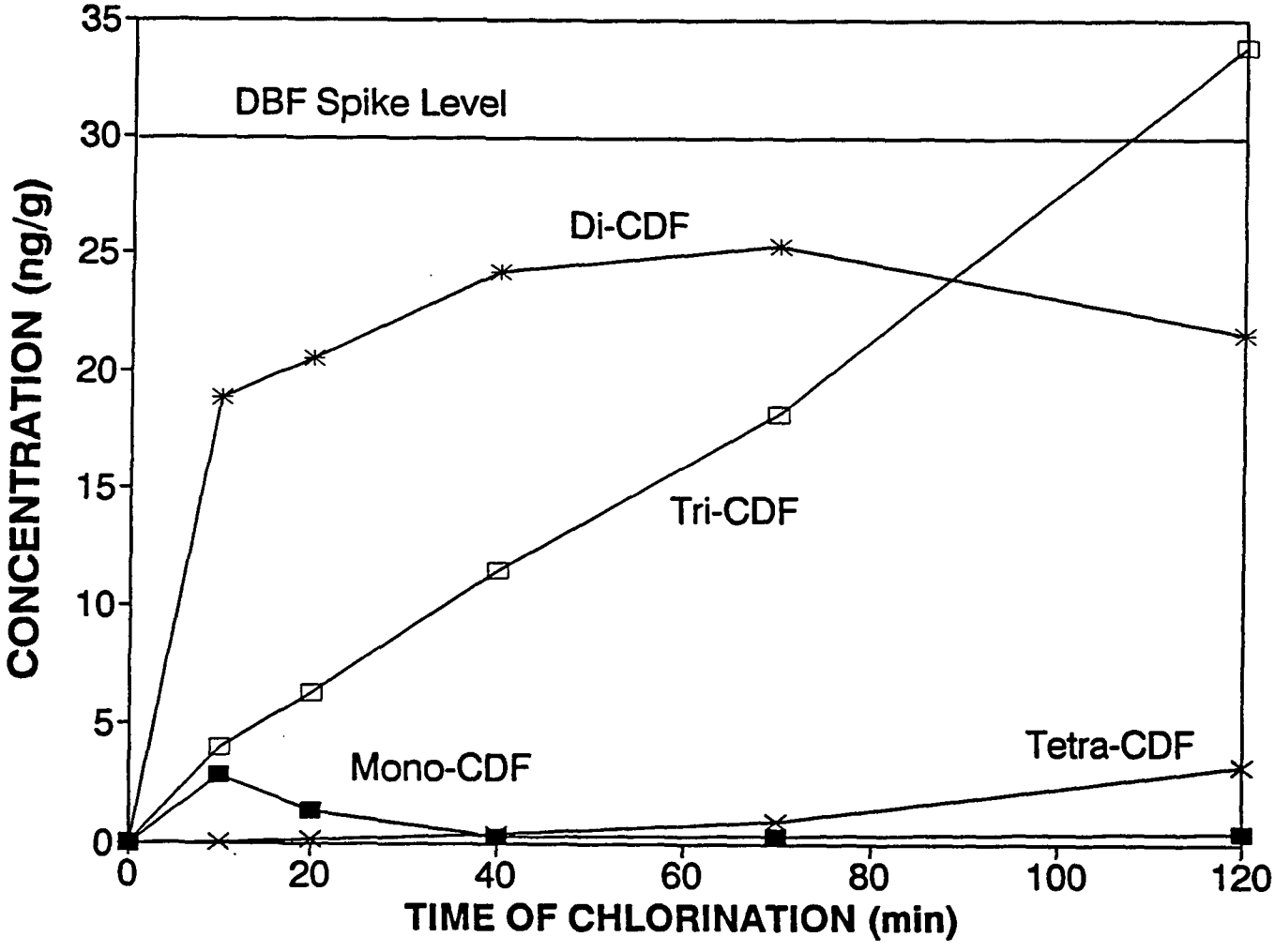

Figure 2. PCDF Formation Upon Chlorination of DBD/F-Spiked Linters

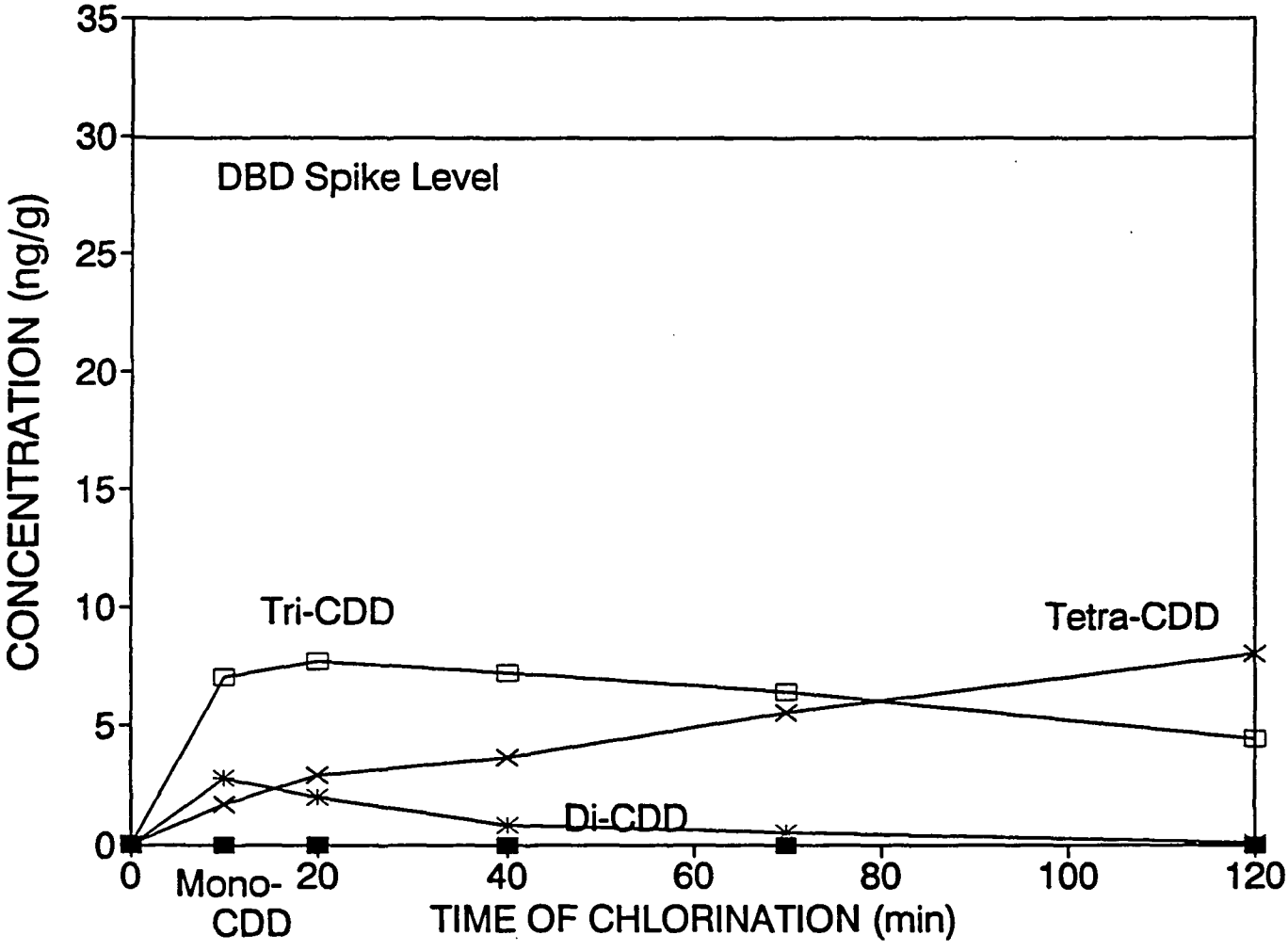

Figure 3. PCDD Formation Upon Chlorination of DBD/F-Spiked Linters

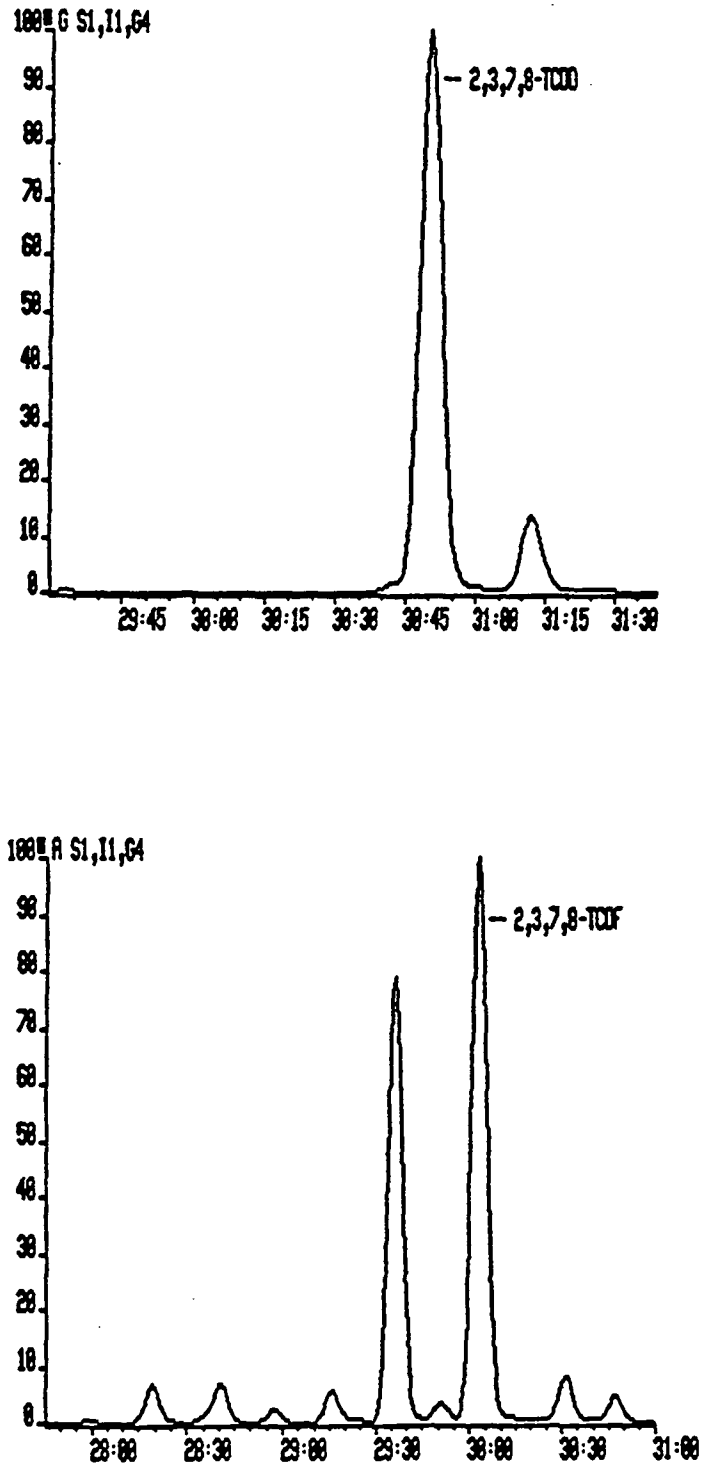

Figure 4. Tetra-CDD/F Isomer Distribution Pattern

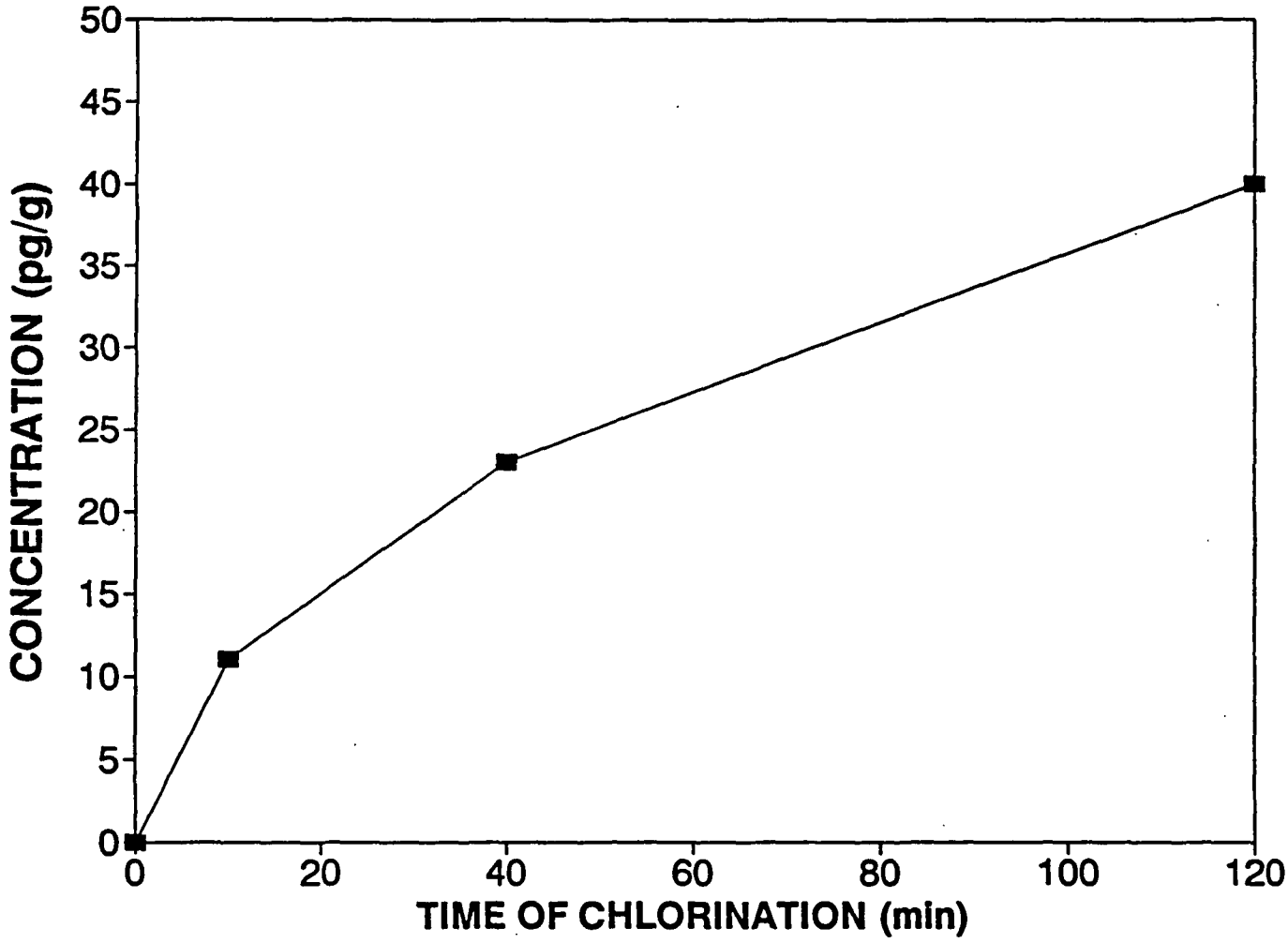

Figure 5. Formation of Tetra-CDD Upon Chlorination of Pre-Extracted Pulp

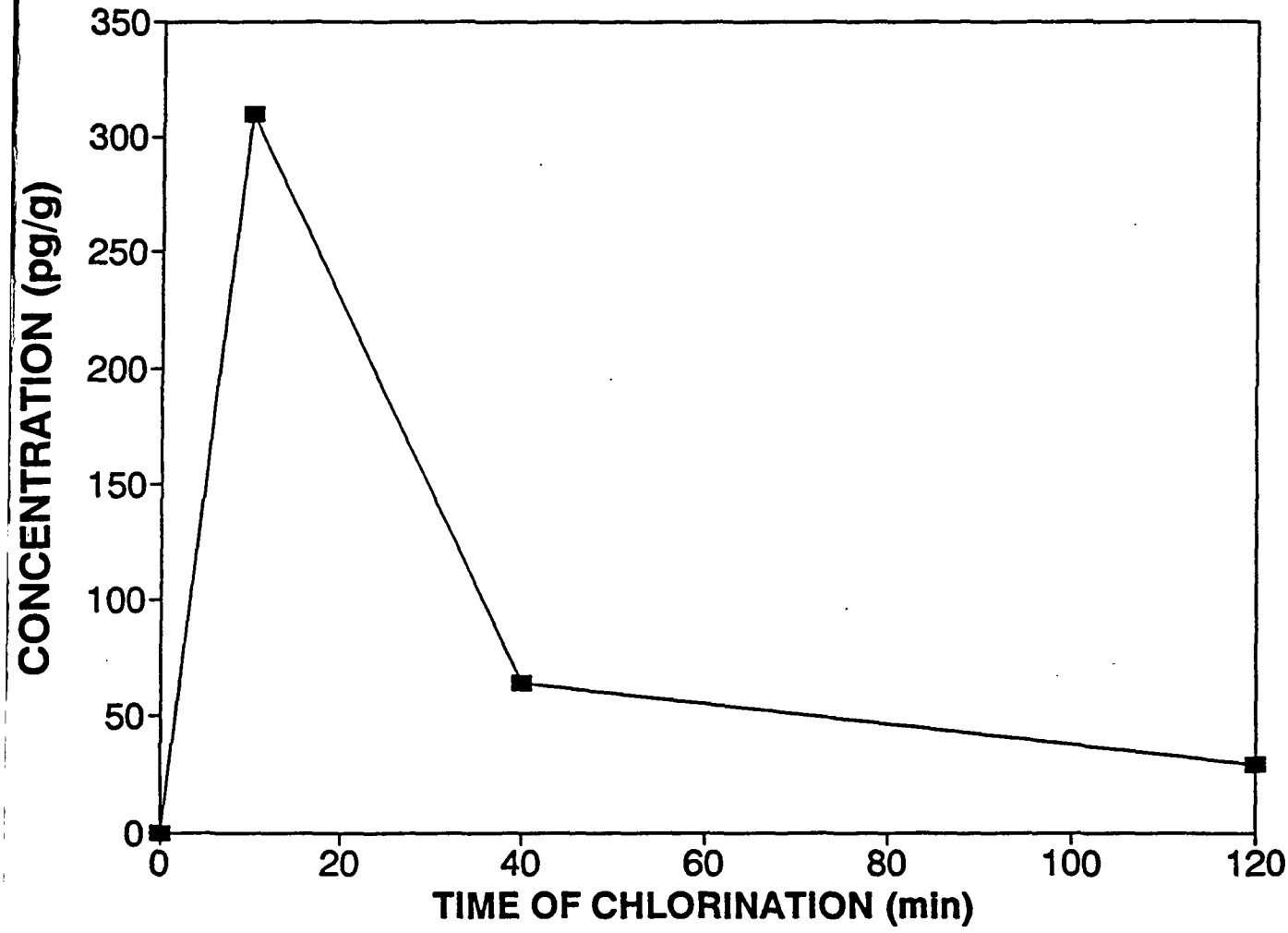

Figure 6. Formation of Mono-CDF Upon Chlorination of Pre-extracted Pulp